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Characterization of network structure of poly(glycidyl azide) elastomers by swelling, solubility and mechanical measurements

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Poly(glycidyl azide) (PGA) networks were prepared by using Desmodur N-100 pluriisocyanate, isophorone diisocyanate (IPDI)/trimethylol propane (TMP), and hexamethylene diisocyanate (HMDI)/(TMP) reactive systems with various NCO/OH reactive group ratios. Swelling tests of these networks were carried out in tetrahydrofuran (THF) at room temperature. The number average molecular weight ($\bar{M}_n$) and polymer solvent interaction parameter (χ_1) of PGA in THF was determined by vapour pressure osmometry (VPO) to be 0.25 for the PGA–THF system at 45°C. The average molecular weights between junction points (M_c) were calculated by using the Flory–Rehner equation. For the networks prepared by three different reaction systems, a linear change of M_c with sol content was observed. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(glycidyl azide) (PGA); glycidyl azide polymer (GAP); swelling; molecular weight between junction points)

INTRODUCTION

The use of polymers as binding materials and fuel in rocket propellant technology is a well-known common practice. The solid propellants are prepared by mixing a functionally terminated polymeric binder with solid particulate oxidizer, plasticizer and other minor ingredients and reacting them with a suitable reactant in order to get physical integrity. The most widely used polymeric binder in propellant technology is hydroxyl terminated poly(butadiene) (HTPB). This can be reacted using di- or plurifunctional isocyanates in the presence of low molecular weight triols (e.g. trimethylol propane, triethanolamine, hexanetriol) via terminal –OH groups. The resultant elastomeric networks have polyurethane structures[1–5].

In addition to the development of new energetic polymers with better specific impulse properties, recently, due to the increasing awareness and sensitivity of environmental problems, an intense demand for chlorine-free propellants has been growing[6–8]. Azide polymers are potential candidates for the preparation of such propellants and contain energetic pendant azide ($-N_3$) groups[9,10]. Poly(glycidyl azide) (PGA) is one of the most important azide polymers synthesized during the last decade and is intended to be a monopropellant with superior combustion properties. It is in fact a high-energetic material with a positive heat of formation, capable of self-burning at elevated pressures. Because of these unique thermal properties, PGA has the ability to offset the poor performance when using ammonium nitrate instead of ammonium perchlorate in the chlorine-free solid propellant composition. These favourable thermal properties of PGA make it a potential candidate for preparing chlorine-free and smokeless propellants with high burning rates and high specific impulses[9].

Poly(glycidyl azide) is a low molecular weight ($\bar{M}_n \cong 2000$), difunctional, hydroxyl terminated liquid prepolymer with a polyether main chain. Therefore, it can be reacted with the –NCO groups of isocyanates and low molecular weight and polyfunctional hydroxyl compounds. The resultant networks also have polyurethane structures.

In the preparation of propellants, the average molecule weight of the network chain (M_c) and density of junction points play an important role in the final physico-mechanical properties.

In the present study, aiming at the development of a smokeless and chlorine-free propellant, attempts were first made at determining the thermodynamic solution properties of PGA–tetrahydrofuran systems and, secondly, at thepreparation and characterization of PGA networks byfollowing their swelling, solubility and mechanical behaviours.

EXPERIMENTAL

Materials

The PGA used in this study was supplied by ICT-Germany. It had a number average molar mass of 1920 g mol^{-1} as determined by vapour pressure osmometry (VPO). The hydroxyl value of PGA was determined as 1.06 mEq g^{-1} using the acetylation method cited in[11]. It was in the form of a viscous liquid with a density of 1.28 g cm^{-3} and a viscosity of 5.1 × 10^3 cP as determined by pychnometry and a Brookfield viscometer, respectively, at room temperature.

Desmodur N-100 pluriisocyanate (compounds containing three or more isocyanate functions are referred to as 'pluriisocyanates') was provided by Bayer and its number average molar mass was determined as 610 g mol^{-1} using

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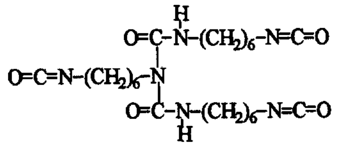
VPO. It had an equivalent weight of 5.24 meq g^{-1}. The idealized molecular formula of Desmodur N-100 was assumed to correspond to the following structure.



Desmodur N-100

Hexamethylene diisocyanate (HMDI) and isophorone diisocyanate (IPDI) were supplied by Fluka, and these were used without further purification. Trimethylol propane (TMP) was used as crosslinker. It was supplied by Aldrich and was used as received.

Instrumentation

The mechanical properties of the PGA networks were measured on a Tensilon (UTM II) tester at room temperature with a crosshead speed of 5 mm min^{-1}. The number average molecular weight of PGA and Desmodur N-100 were determined using a Knauer Vapour Pressure Osmometer. The Flory–Huggins interaction parameter of the PGA–THF system was also calculated from VPO data obtained at 45°C in THF.

Preparation of poly(glycidyl azide) elastomers

For the purpose of observing the effect of type of reactive system and the change in NCO/OH group ratio on the physico-chemical properties of PGA networks, three different sets of formulations with different NCO/OH ratios were prepared. These formulations are gathered in *Table 1*.

In the first set, Desmodur N-100 pluriisocyanate was used as the curing agent. In the second and third sets, IPDI and HMDI were used as curing agents, respectively. In the last two compositions, TMP was used as the crosslinking agent and, since mechanical properties were best at an equivalent ratio of $OH_{(triol)}/OH_{(triol)} + OH_{(diol)} = 0.4$, this ratio was kept constant as 0.4 in these two formulations[3,6].

For the preparation of PGA elastomers using TMP, a calculated amount of TMP was dissolved in previously degassed PGA at 65°C and mixed for 15 min under 200 mmHg vacuum. Then diisocyanate was added. After mixing for 3 min, the viscous liquid was cast into a Teflon-coated mould to form a film of 1–1.5 mm thickness. The resin was cured in a nitrogen atmosphere at 65°C for 7 days. The preparation of PGA networks using Desmodur N-100 was performed without TMP by a procedure similar to that described above[12].

Determination of equilibrium swelling

Swelling experiments were performed to determine the average molecular weight between junction points (M_c) for different PGA networks with different junction point densities. These networks were prepared by using different isocyanates, i.e. isophorone diisocyanate, hexamethylene diisocyanate and Desmodur N-100 pluriisocyanate.

Swelling measurements were carried out in THF at room temperature and the volume fraction of PGA at equilibrium

Table 1 Composition of PGA networks prepared by using three different reactive systems

	Composition I (wt%)		Composition II (wt%)			Composition III (wt%)		
NCO/OH ratio	PGA	N-100	PGA	TMP	IPDI	PGA	TMP	HMDI
1.05	82.475	17.525	80.788	2.550	16.662	84.213	2.659	13.128
1.00	83.169	16.831	81.434	2.571	16.000	84.743	2.676	12.581
0.95	—	—	82.08	2.592	15.319	85.279	2.693	12.028
0.90	84.593	15.407	—	—	—	85.823	2.710	11.468
0.80	86.066	13.934	84.125	2.656	13.219	—	—	—
0.70	87.59	12.408	—	—	—	—	—	—

Table 2 Swelling, solubility and mechanical measurement results of PGA elastomers prepared using Desmodur N-100, IPDI/TMP and HMDI/TMP mixtures as network forming systems

	NCO/OH reactive group ratio	M_c (g mol^{-1})	Sol fraction (wt%)	Elongation at break (%)	q_v
Desmodur N-100	1.05	1990	2.51	89	3.80
Desmodur N-100	1.00	2220	2.80	90	3.87
Desmodur N-100	0.90	2590	4.38	112	4.14
Desmodur N-100	0.80	4050	8.96	158	5.12
Desmodur N-100	0.70	5580	15.25	167	5.99
IPDI/TMP	1.05	6080	3.15	177	6.25
IPDI/TMP	1.00	7300	8.98	184	6.85
IPDI/TMP	0.95	7850	10.18	185	7.10
IPDI/TMP	0.80	15200	31.84	498	10.01
HMDI/TMP	1.05	4700	5.64	150	5.50
HMDI/TMP	1.00	5780	7.48	168	6.09
HMDI/TMP	0.95	6500	7.75	175	6.45
HMDI/TMP	0.90	7150	9.30	190	6.77

was determined gravimetrically. Small pieces of PGA elastomers weighing about 0.3–0.4 g were immersed in THF, and swollen gels were removed from solvent at different times, quickly blotted with dry filter paper and weighed. The equilibrium swelling ratio of the PGA elastomers and the volume fraction of polymer can be calculated by assuming the additivity of volumes, using the following equations.

$$q_v = 1 + (w_2/w_1 - 1)\rho_2/\rho_1$$

$$\nu_{2m} = 1/q_v$$

where w_2 is the weight of the specimen at equilibrium, w_1 is the weight of the specimen before swelling, q_v is swelling ratio of the network by volume, ν_{2m} is the volume fraction of polymer in the gel at equilibrium and ρ_1 and ρ_2 are thedensities of solvent and polymer, respectively (0.889 g cm^{-3} for THF and 1.28 g cm^{-3} for PGA prepolymer at room temperature). The equilibrium swelling ratios of PGA elastomers are listed in *Table 2*.

Determination of sol–gel content

The sol–gel contents of the PGA elastomers were determined by extraction of the sol fractions. Samples weighing 0.3–0.4 g from each preparation recipe (w_1) were immersed in THF for 24 h and in chloroform for 24 h. Poly(glycidyl azide) elastomers were deswollen in acetone–methanol mixtures, dried under 200 mmHg vacuum at 50°C and weighed (w_2)[13]. The weight difference between w_2 and w_1 was taken as the weight of the sol. The sol fractions of PGA elastomers are listed in *Table 2*.

RESULTS AND DISCUSSION

Determination of M_c *values of poly(glycidyl azide) elastomers*

The average molecular weight of the chain sections between crosslinks M_c, and the degree of crosslinking are very important factors for the characterization of three-dimensional networks. M_c values were determined from the swelling measurements of PGA elastomers through the application of the Flory–Rehner equation. The swelling of crosslinked elastomers was followed gravimetrically and the kinetics of swelling are given for a system prepared by IPDI with various reactive group ratios in *Figure 1*. Some differences were observed both in the rate and in the equilibrium value of swelling, depending on the type of crosslinking system used in the preparation of the network. The volume of the swollen network prepared with the same ratio of NCO/OH was observed to be the highest with IPDI and lowest with Desmodur N-100. The swollen volumes reached at equilibrium were used in the determination of M_c values through the Flory–Rehner equation. Before attempting to use this equation, the χ_1 parameter for the PGA–THF system was determined by using VPO. It has been pointed out that VPO can be a suitable experimental technique for measuring the thermodynamic properties of polymer–solvent systems, and, as reported in the literature, the χ_1 parameter can be calculated according to the following equation[14,15].

$$-\Delta R M_1/1000\,K = \ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2 \quad (1)$$

where M_1 is the molecular weight of the solvent, ΔR is the electrical resistance recorded from VPO, K is the calibration constant of the osmometer, which was determined using benzyl (MW = 210) as calibration substance, ν_2 is the volume fraction of polymer, x is the number of chain segments in a polymer molecule, the segments having approximately the same volume as a solvent molecule, and χ_1 is the Flory–Huggins interaction parameter of the polymer–solvent system. Regarding the data obtained from VPO and using equation (1), the polymer–solvent interaction parameter, χ_1 for the PGA–THF system was calculated as 0.25 at 45°C.

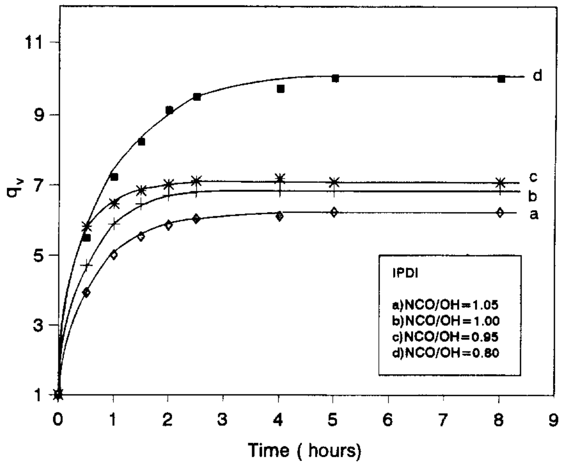


Figure 1 Typical swelling behaviour of PGA networks prepared by IPDI/TMP system in THF

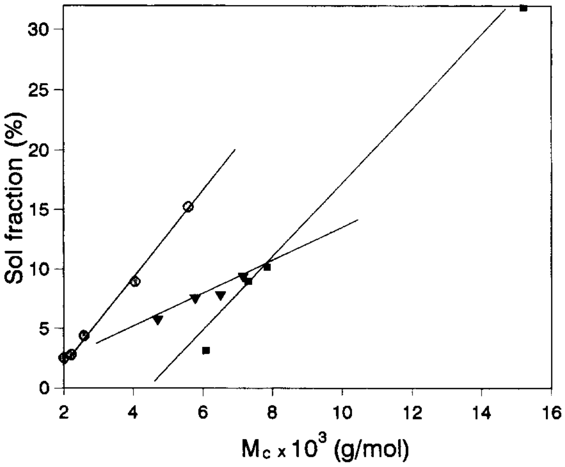


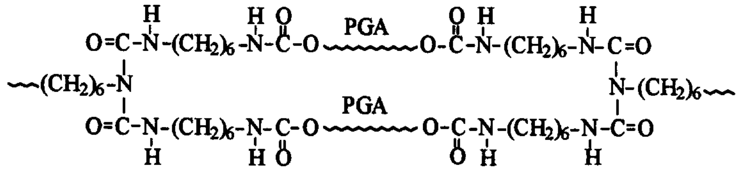
Figure 2 The relationship between M_c and sol fraction of PGA elastomers prepared by using three different reactive systems: ○, Desmodur N-100; ■, IPDI/TMP; ∇, HMDI/TMP

The M_c values of the PGA elastomers were calculated using the Flory–Rehner equation[16–19].

$$M_c = -V_1\rho(v_{2m}^{1/3} - v_{2m}/2)/[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_m^2] \quad (2)$$

where M_c is the average molecular weight between junction points, ν_1 is the molar volume of solvent, ρ is the density of the PGA network and v_{2m} is the volume fraction of polymer in swollen gel at equilibrium. In this work, the χ_1 parameter was calculated at 45°C and all the swelling experiments were performed at room temperature. It was observed that the swelling values remained unchanged over the temperature range between room temperature and 45°C. This can be interpreted as that χ_1 is relatively insensitive to temperature over this temperature range. The M_c values of the PGA elastomers determined through equation (2) are shown in *Table 2*. If we consider the data given in *Table 2*, it can be clearly seen that the chain length between junction points, M_c, is strongly effected by the type of reaction system and the NCO/OH group ratio. For the same NCO/OH ratio, Desmodur N-100 cured elastomers have smaller M_c values than those of IPDI/TMP and HMDI/TMP cured elastomers. The junction-point densities in each of the three systems are determined by the proportions of polyfunctional reactants (Desmodur and TMP). Also, chain extension and branching occur simultaneously in all three systems, not just those with TMP. What is different is that the polyfunctional reactant in the Desmodur systems is not mixed (diluted) with difunctional reactant having the same type of reactive group.

Assuming that the network structure obtained with Desmodur N-100 at NCO/OH = 1 equivalent ratio is that of the ideal network, its structure can be represented as follows:



From the swelling experiments, the M_c value of the network is calculated as 2220 (*Table 2*). If we take into account the contribution of HMDI part of Desmodur N-100 and the number average molecular weight of the PGA prepolymer, the M_c value calculated for such a chain section is 2260. This calculated value is nearly the same as the experimentally determined value. In spite of the approximations involved both in the Flory–Rehner equation and in the determination of the χ_1 parameter, the agreement between these two values is striking.

In conformity with the results obtained for M_c, as the NCO/OH ratio is increased, the swelling ratio (q_v) and sol fraction decrease. As can be seen from *Table 2*, a trend is apparent when the elongation at break values are compared with the data obtained from swelling experiments; with increasing M_c, elongation also increases. This means that the longer the chain length between junctions, the more elastic is the network, the greater the quantity of sol fraction and the larger the swelling.

From the data gathered in *Table 2*, it is clearly observed that the sol fraction of network is directly related to the average chain length between junctions (M_c). Over all compositions, the sol fraction increases as M_c increases. It is interesting to note that the correlation between M_c and sol fraction is almost linear. These relationships between M_c and sol fraction of PGA networks prepared by using the three different reaction systems are illustrated in *Figure 2*. They can be explained on the basis of some PGA chains not being reacted. With NCO/OH ratio decreasing from one, the PGA chains become more and more end-linked rather than intermolecularly linked. Although end-linking will lead to more chain extension with subsequent increase in molecular weight, since they are not incorporated into a three-dimensional network structure, the soluble part increases. It is interesting to observe the linear relationship between % sol fraction and M_c.

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